UNIVERSITY OF PENNSYLVANIA

STUDIES ON THE PREPARATION OF GERMANIUM AND CERTAIN OF ITS COMPOUNDS

EDWIN FREDERIC PIKE

A THESIS

IN CHEMISTRY

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

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PART I

The Behavior of Aqueous Solutions of Germanium Dioxide With the Alkaline Earth Metals

In Winkler's original article concerning germanium,[1] he pointed out the possible existence of the acid $GeO(OH)_2$ as well as the normal acid $Ge(OH)_4$, but compounds of these types had not been reported as yet. Recently, Müller[2] prepared and described magnesium orthogermanate and discussed its use in the gravimetric determination of germanium. This communication will show the existence of derivatives of both ortho- and metagermanic acid. In addition, the behavior of some bivalent elements, other than the alkaline earths, with solutions of germanium dioxide will be discussed.

Reagents and Apparatus

Calcium Nitrate. Calcium nitrate was prepared by dissolving calcspar in pure nitric acid free from sulphuric acid and iron, and then boiling the resulting solution under reduced pressure to remove all traces of carbon dioxide.

Barium Nitrate. Barium nitrate was made by recrystallizing barium chloride five times from a solution saturated with hydrochloric acid and discarding all but the middle fraction each time. The barium chloride was converted to the nitrate with nitric acid and then recrystallized.

Strontium Nitrate. Strontium nitrate was prepared by repeated recrystallization of analytical grade strontium nitrate.

Ammonium Hydroxide. The best commercial grade ammonium hydroxide was dropped into a strong solution of potassium hydroxide and the evolved gas was absorbed in cooled, freshly distilled, carbon dioxide free water.

Germanium Dioxide. The germanium dioxide used was of the

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[1] Winkler: *Jour. Prak. Chem.*, 34, 213 (1886).
[2] Müller: *Jour. Amer. Chem. Soc.*, 44, 2493 (1922).

highest purity and free from arsenic. The solutions used varied in concentration and never exceeded 0.0050 g. GeO_2 per c.c. The concentrations of the various solutions were determined by evaporating 50 c.c. to dryness and igniting the residual germanium dioxide to constant weight over the blast lamp.

Hydrochloric Acid. The acid was of the grade known as "C.P." and contained 36 to 38 per cent of HCl.

Sulphuric Acid. The sulphuric acid was "C.P." grade (containing 98.09 per cent H_2SO_4 and free from arsenic).

Ethyl Alcohol. The alcohol was prepared by allowing 95 per cent ethyl alcohol to stand over fresh lime for two days and then distilling over lime. The dehydration was completed by the use of a small amount of metallic sodium after which the alcohol was fractionally distilled.

Ether. Ethyl ether was allowed to stand over metallic sodium for twenty-four hours and then fractionally distilled.

Carbon Disulphide. The carbon disulphide was redistilled and the fraction boiling between 46 and 47 C. used.

The water was freshly distilled and freed from carbon dioxide by prolonged boiling under reduced pressure.

Experimental

Forty c.c. of an aqueous solution of germanium dioxide containing 0.1620 g. of the oxide were treated with 15 c.c. of a solution containing 0.58605 g. of calcium nitrate and to this mixture were added 50 c.c. of ammonium hydroxide. A dense milkyness appeared and the mixture was then boiled, using a Bunsen valve to exclude air. The mixture was maintained at the boiling temperature for five minutes. The dense, white, gelatinous precipitate which formed was allowed to settle and stand for twelve hours. Attention should be directed to the appearance of the precipitate. When the calcium nitrate and the germanium dioxide solutions were mixed in the ratio of two molecules of the former and one molecule of the latter, and an equal volume of strong ammonium hydroxide added, the precipitate formed was extremely bulky and had the appearance of shredded filter paper. The rapid settling of the precipitate is usually indicative of the salt whose formula will be shown to correspond to $CaGeO_3$.

If, however, the germanium dioxide be used in excess over calcium nitrate and more than twice the volume of strong ammonium hydroxide be added and the solution just brought to incipient boiling in the absence of air, the precipitate does not settle rapidly on standing. The formula of this salt will be shown to be Ca_2GeO_4. Care must be taken to bring the solution just to incipient boiling in the preparation of the ortho-salt. The absence of air must be insured in order that calcium carbonate may not be formed and weighed along with the germanate. A Bunsen valve was used to prevent contact with the air during the preparation of these salts.

If the solutions of germanium dioxide and calcium nitrate are sufficiently concentrated, the precipitate of the calcium salt will form a solid gel on standing. For example, if the salt is prepared as described in the instance first given above and a slight excess of ammonia distilled into the mixture, a solid gel results. The precipitates of both the ortho and meta calcium salts are so bulky that very small amounts of germanic acid can be detected in this way. As little as 0.00012 g. of germanium dioxide in 25 c.c. of solution has been detected. It was found that calcium chloride could not be used in the preparation of the calcium germanates due to the formation of ammonium chloride which is carried down with the precipitate of the calcium salt. On heating the salt so prepared, germanium is lost as the volatile chloride.

The action of barium nitrate with solutions of germanium dioxide was next studied. 50 c.c. of a solution containing 3.6550 gms. of barium nitrate were added to 100 c.c. of a solution containing 0.4870 g. of germanium dioxide and to this mixture were added 200 c.c. of ammonium hydroxide. The addition of the ammonium hydroxide caused an immediate turbidity, and when the solution was boiled for five minutes, a dense, white precipitate was formed which settled rapidly. The precipitate was allowed to stand over night and on analysis was found to correspond to $3CaO$, $5GeO_2$. Analysis of the barium salt so prepared gave the results found in Table I but sufficient data has not yet been obtained to make certain the definiteness of this compound.

The strontium salt was prepared in a manner analogous to that used for the calcium salts. 100 c.c. of a solution containing 2.950 gms. of strontium nitrate were added to 100 c.c. of a solution containing 0.487 g. of germanium dioxide and after adding 200 c.c. of ammonium hydroxide, the solution was boiled for five minutes using a Bunsen valve. The precipitated salt was dense and pure white and did not settle so quickly as the barium salt nor so gradually as the calcium salts. It was found that the calcium salts showed a greater tendency to gel formation than either the barium or strontium salts.

The action of certain other metallic nitrates with aqueous solutions of germanium dioxide will be discussed later.

Composition and General Properties of the Precipitates

The precipitates obtained in the manner described above were analyzed as follows:

After thorough washing with water and ignition to constant weight over a Meker burner and finally over a blast lamp, the white infusible mass was transferred to a 500 c.c. Pyrex distilling flask and distilled with 180 c.c. of 6N. hydrochloric acid until approximately 30 c.c. of the solution remained in the flask. The distilling bulb was fitted with a bent delivery tube which passed through a water jacket and barely came in contact with the surface of the water in the receiver. The receiver was chilled thoroughly to prevent loss of the germanium. The distillate was made approximately 6N. by concentrated hydrochloric acid and the acid solution was saturated with hydrogen sulphide under pressure. The precipitated germanium sulphide was filtered. When the germanium was to be determined as oxide, the sulphide was filtered on quantitative paper and the filter with the precipitate carefully treated with strong nitric acid in a weighed crucible. The oxidation of the sulphide with nitric acid proceeds actively and care was taken not to lose germanium by spattering. The germanium sulphide was taken to dryness three times with nitric acid and strongly ignited to constant weight.

Most of the determinations of germanium were made by weighing the metal as sulphide. Accordingly, the precipitate of germanium sulphide as received on a weighed Gooch filter was washed with 20 c.c. of 1:1 sulphuric acid that had been completely saturated with hydrogen sulphide. This washing removes any residual hydrochloric acid. The sulphuric acid was washed out of the precipitate with 10 c.c. of absolute alcohol saturated with hydrogen sulphide and this was followed with the same volume of carbon disulphide saturated with hydrogen sulphide. Alcohol and ether saturated with the same gas were used successively to complete the washing of the precipitate. The thoroughly washed precipitates were dried in an electric oven at 105 C. and then weighed.

The solution remaining in the flask containing the alkaline earth chlorides was transferred to a weighed crucible and taken almost to dryness when a little dilute sulphuric acid was added and the whole taken to dryness. The residue was evaporated with concentrated sulphuric acid and then ignited to constant weight over a Meker burner and finally over a blast lamp. The sulphates were weighed as such. After weighing, they were evaporated to dryness with concentrated hydrochloric acid and reignited and weighed. Any loss in weight was due to germanium that had been carried along with the alkaline earth metal.

Difficulty is met in obtaining complete separation of the germanium from its associated metal by the distillation method described. In the case of the barium salt, the separation is especially difficult. As the volume of the solution in the distilling flask becomes small, the barium chloride begins to precipitate due to the fact that, in addition to the small volume, the solution is saturated with hydrogen chloride. The barium chloride thrown down carries germanium with it which is removed with difficulty in the further treatment to determine the barium. Some additional sources of error will be discussed later. The results obtained by the analytical methods described above were as follows:

TABLE I

Compound	Weight of salt	MeO Found	GeO_2 Found	MeO calculated	GeO_2 calculated
		Per cent	Per cent	Per cent	Per cent
$CaGeO_3$...	0.2216	35.32	66.21	34.93	65.07
	0.2216	34.56	65.44*	.....	.....
	0.3012	35.60	64.40*	.....	.....
	0.7176	35.82*	64.18	(* = by difference)	
	0.3972	35.84	64.16*		
		Av. = 35.43	Av. = 64.88		
Ca_2GeO_4...	0.0594	51.68*	48.32	51.77	48.23
	0.3535	51.24	48.76*		
		Av. = 51.46	Av. = 48.54		
$SrGeO_3$....	0.1279	50.20	49.80*	49.79	50.21
	0.1279	49.34*	50.66		
		Av. = 49.77	Av. = 50.23		
$3BaO,-5GeO_2$...	0.2590	46.78	53.22	46.82	53.18
	0.5666	45.61	54.32		
		Av. = 46.20	Av. = 53.77		

The calcium, barium, and strontium salts obtained as described above are pure white, amorphous substances and show no crystalline structure upon microscopic examination. They are infusible at the highest temperature obtainable with the blast lamp and are non-volatile at a white heat. The freshly prepared and thoroughly washed salts are readily soluble in the dilute mineral acids from which the alkaline earth sulphates are precipitated by addition of sulphuric acid. After ignition, the salts are slowly dissolved by the dilute mineral acids. They are insoluble in strong caustic potash but are slowly dissolved by a concentrated solution of sodium carbonate at the boiling

temperature with the formation of the alkaline earth carbonate. An effort was made to use this last fact in the analysis of the salts but it met with little success.

Discussion

The formation of the calcium salt of meta-germanic acid was somewhat unexpected since the only previously reported germanate of a metal nearly approaching calcium in basicity was the magnesium ortho-germanate. And, strangely enough, the meta salt is the one ordinarily formed for, in the preparation of a salt of this kind, an excess of the more common alkaline earth is usually added. It remained to show how the meta salt might be produced. Theoretically, calcium meta-germanate can result from the following reactions:

1. $Ca(NO_3)_2 + GeO_2 + 2NH_4OH = CaGeO_3 + 2NH_4NO_3 + H_2O$
2. $Ca(NO_3)_2 + GeO_2 + 2NH_4OH = CaH_2GeO_4 + 2NH_4NO_3$
   $CaH_2GeO_4 = CaGeO_3 + H_2O$
3. $Ca(NO_3)_2 + GeO_2 + 4NH_4OH = Ca(NH_4)_2GeO_4 + 2NH_4NO_3 + 2H_2O$
   $Ca(NH_4)_2GeO_4 = CaGeO_3 + 2NH_3 + H_2O$

According to equation 1, the salt is formed in exactly the same way as calcium carbonate and is thrown out of solution in the strong alkaline environment.

Equation 2 shows the salt as resulting from the calcium acid orthogermanate by removal of water. Since the meta salt is made by boiling vigorously the solution in which the salt is being thrown down, it might be inferred that the acid salt was first formed and that the boiling caused the removal of the molecule of water. Using the excess of the calcium nitrate indicated above in the discussion of the calcium metagermanate and adding the ammonium hydroxide as before and allowing the mixture to stand in the cold for several days, a salt resulted that had the same composition as before.

Ignition of the salt after precipitation might offer the means of separating the molecule of water from the acid salt. To determine if this were true, a portion of the freshly prepared and well-washed salt was dried as much as possible on a Buchner

funnel. The salt was allowed to stand in a vacuum dessicator over concentrated sulphuric acid for several weeks and weighed periodically. No definite removal of water could be detected that would correspond to that required by the assumption made.

Equation 3 indicates the intermediate formation of an ammonium salt which would subsequently lose two molecules of ammonia and one molecule of water to give the meta salt. A portion of the freshly prepared salt was washed with water until the free ammonia was removed. The residual air-dried salt was tested for the ammonium radical with hot caustic alkali. A negative result was obtained. It appears that the calcium meta-germanate is the most stable calcium salt of germanic acid and that it is probably formed directly as such.

The action of a solution of germanium dioxide with other bivalent metals was studied under conditions that were comparable to those under which the alkaline earth germanates were produced.

Two hundred and ten c.c. of a solution of cobalt nitrate containing 0.4402 g. of the salt were mixed with 33.44 c.c. of a solution containing 0.193 g. of germanium dioxide, and to the mixture, 300 c.c. of strong ammonium hydroxide were added and the whole boiled four minutes. Air was excluded by a Bunsen valve. On standing in a sealed flask for two days, the solution had deposited nothing.

Similarly, 0.3408 g. of nickel nitrate in 125 c.c. of water were mixed with 40 c.c. of a solution containing 0.195 g. of germanium dioxide, and 10 c.c. of ammonium nitrate and after addition of 175 c.c. of strong ammonia, the whole was boiled using a Bunsen valve. A blue solution resulted. There was no deposit found in the flask after standing three days. The ammonia was boiled off the solution and the blue color changed to green. On adding ammonia until the solution was just basic, the blue color was restored but no precipitate formed on standing in a stoppered flask for four days.

Fifty c.c. of a solution containing 1.4 g. of mercuric chloride were added to 50 c.c. of a solution containing 0.195 g. of germanium dioxide. This mixture was boiled for five minutes in a flask fitted with a Bunsen valve and allowed to stand five days.

No precipitate resulted. 0.804 g. of freshly precipitated mercurous oxide was washed free from alkali and then treated with 50 c.c. of a solution containing 0.195 g. of germanium dioxide and boiled for one-half hour adding water from time to time to replace that evaporated. On standing over night, the solution deposited nothing. The solution was then evaporated to a volume of 10 c.c., and allowed to evaporate spontaneously to a volume of about 2 c.c., but no definite mercury compound was obtained.

The Hydrolysis of Germanium Disulphide and Some Observations on the Errors Introduced In the Determination of Germanium As Sulphide

It was observed by Winkler[3] that the solubility of germanium sulphide in pure water was fairly close to that of the dioxide in the same solvent. One part of dioxide was stated to dissolve in 247.1 parts of water at 20 C., while one part of germanium disulphide required 221.0 parts of water presumably at the same temperature. Müller[4] noticed the conversion of the sulphide to the dioxide by water at the boiling point. Winkler also observed that the drying of germanium sulphide was accompanied by an evolution of hydrogen sulphide. From these observations it would appear that the sulphide may be more or less completely hydrolyzed by boiling water and a study of the behavior of germanium disulphide with boiling water was therefore made.

The germanium disulphide for this purpose was prepared by dissolving germanium dioxide of the highest purity in pure, freshly distilled water. This solution was made 6 N. with concentrated hydrochloric acid. The solution was then saturated with hydrogen sulphide under pressure and the precipitated sulphide was filtered through ordinary quantitative filter paper and washed with 1:1 sulphuric acid saturated with hydrogen sulphide. It was then washed successively with alcohol, carbon

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[3] Winkler: *Jour. Prak. Chem.*, 34, 213 (1886).

[4] Müller and Iszard: *Jour. of Metabolic Research*, 3, 1–197 (1923).

disulphide, alcohol, and finally with ether, all of the washing agents being thoroughly saturated with hydrogen sulphide. The germanium sulphide was then washed with dry air in a vacuum desiccator and finally dried over calcium chloride under reduced pressure. The hydrogen sulphide used was prepared from antimony sulphide and hydrochloric acid which was free from arsenic. All other reagents used were those prepared as described in Part 1 of this paper.

Procedure

Pure freshly distilled water was boiled in an Erlenmeyer flask for a sufficient time to expel all air from the flask. The water was kept boiling vigorously and a small bottle containing a weighed amount of germanium sulphide was introduced. The quantity of water in the flask was such that the germanium sulphide did not exceed 0.00654 g. per c.c. of water. It was convenient to use an amount of water in excess of that required for the above concentration.

An immediate and vigorous evolution of hydrogen sulphide took place. Care was taken when the sulphide was introduced in the boiling water to prevent the steam and hydrogen sulphide evolved from scattering the very light and finely divided material. The boiling was continued until the solution in the flask was perfectly clear and at the same time a negative test for hydrogen sulphide was found in the escaping steam. Fifty minutes of boiling were sufficient to give a clear solution when 1.6110 gms. of germanium sulphide were used. The solution was transferred to a calibrated flask and made up to 250 c.c. with pure water.

One hundred c.c. of the above solution were evaporated to dryness on a water bath with 20 c.c. of concentrated nitric acid. The residue was then taken up in 125 c.c. of water and filtered. To the filtrate, barium chloride was added and the whole allowed to stand over night. The trace of barium sulphate found was ignited and taken to dryness twice with concentrated hydrochloric acid to remove any germanium that might have been carried down with it and then reignited and weighed. The following results were obtained:

GeS_2 taken gms.	$BaSO_4$ found gms. per c.c.	GeO_2 calculated gms. per c.c.	GeO_2 found gms. per c.c.
1.6110	0.0000186	0.00493	0.00488

From this it will be seen that germanium sulphide prepared with hydrogen sulphide from stibnite and arsenic-free hydrochloric acid as outlined above, hydrolyzes completely in boiling water. The fact that germanium sulphide is so readily hydrolyzed to oxide by water explains why these two compounds have nearly the same solubility for more or less of the dioxide is produced by hydrolysis.

Mention was made earlier in this paper of the difficulties encountered in the determination of germanium as sulphide. The precipitation of germanium sulphide has been shown to be complete.[5] Therefore, sources of error in the sulphide determination are probably found in the methods of preparation of the sulphide for weighing. The sulphide is usually precipitated from a solution acid with sulphuric acid or hydrochloric acid and the precipitate must be freed, therefore, of the water and the acid. If hydrochloric acid is used, washing with 1:1 sulphuric acid serves to remove it but leaves dilute sulphuric acid in its stead. The sulphide is next washed with alcohol saturated with hydrogen sulphide for the purpose of removing the water. A milky filtrate invariably results. Running the filtrate through the filter repeatedly fails to give a clear solution. This first washing with alcohol is followed by a washing with carbon disulphide saturated with hydrogen sulphide to remove any free sulphur in the germanium sulphide. The sulphide must be reasonably free from water else the carbon disulphide will not remove the free sulphur completely. A second washing with alcohol is used to remove the carbon disulphide, and finally, ether saturated with hydrogen sulphide used to complete the preparation of the sulphide for drying. The sulphide is dried in an oven at 105 C.

A series of experiments was made to determine the effect of the reagents used in washing the germanium sulphide so as to

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[5] Winkler: *Jour. Prak. Chem.*, 34, 213 (1886).

discover the nature and amount of the error attributed to each operation. Anhydrous alcohol was saturated with hydrogen sulphide under pressure as were also water-free ether and carbon disulphide. These reagents were placed in glass tubes of 20 c.c. capacity suspended in a thermostat maintained at 25 C. Into the several tubes, pure germanium sulphide was allowed to remain in contact with the above reagents for twenty-four hours. Similar tubes were prepared containing the above reagents without hydrogen sulphide. The tubes were shaken frequently. The contents of the tubes were filtered through dry filter paper in a closed vessel to prevent evaporation and a definite volume of each was evaporated to dryness with nitric acid twice and then ignited to constant weight over a blast lamp and weighed as germanium dioxide. The following table shows the amount of germanium sulphide dissolved by the several washing agents used, in grams per c.c.

Material	Amount of GeS_2 dissolved calculated as GeO_2. Gms. per c.c.
CS_2 saturated w. H_2S	0.00000
Ether saturated w. H_2S	0.00000
Alcohol saturated w. H_2S	0.00005
CS_2	0.00004
Ether	0.00003
Alcohol	0.00005

From the above table, it will be seen that carbon disulphide and ether saturated with hydrogen sulphide have no appreciable effect or solvent action on germanium disulphide but the alcohol, even though saturated with hydrogen sulphide, does have some action. Inasmuch as the amount of alcohol used to wash 0.300 g. of germanium sulphide usually amounts to at least 40 c.c., it will be seen that the loss of sulphide by this means is considerable.

PART II

The Behavior of Germanium When Heated in Hydrogen

Winkler[6] found that germanium dioxide was reduced by the action of hydrogen at a red heat, but stated that the reduction was not complete. Müller[7] attempted to determine the atomic weight of germanium by using the GeO_2 : Ge ratio when the oxide was reduced in hydrogen and stated that the "results were very unsatisfactory for two reasons. First, the purity of the oxide was questionable," and "the hydrogen stream carried over small quantities of metal as hydride." "This was proved by washing the waste hydrogen in a solution of a silver salt when a small black deposit was slowly formed which contained silver germanide and metallic silver. It was noted that the reduction to metal proceeded to completion at 700 degrees." "Every heating in hydrogen at this temperature, however, caused further loss in weight." In a later article,[8] he states that "metallic germanium is slowly but appreciably volatile in hydrogen at elevated temperatures."

Dennis[9] states that the reduction of small amounts of germanium dioxide of the magnitude of 0.35 g. by heating in hydrogen at 500 to 540 C. is complete within two hours, and "that no volatility of germanium or of any compound of the element takes place under these conditions." In the same article, he concludes that "metallic germanium which is free from oxide does not lose weight when heated in hydrogen to a temperature not exceeding 800 degrees, but that volatilization does take place when hydrogen is passed over the molten metal."

Since there seems to be some disagreement in the above results, the following investigation was undertaken:.

Apparatus and Materials Used

The germanium dioxide used in this work was prepared by frequent redistillation of the tetrachloride and followed by hydrolysis of the latter in pure water. The oxide was entirely free from arsenic and metals other than germanium, and upon

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[6] Winkler: *Jour. Prak. Chem.*, 34, 202 (1886).
[7] Müller: *Jour. Amer. Chem. Soc.*, 43, 1086 (1921).
[8] Müller: *Jour. Amer. Chem. Soc.*, 45, 2035 (1923).
[9] Dennis, Tressler and Hance: *Jour. Amer. Chem. Soc.*, 45, 2037 (1923).

hydrolysis of the chloride, yielded a product containing only a trace of chlorine. The final purification of the oxide for the removal of the last traces of the chlorine was brought about by protracted ignition in an atmosphere of superheated steam, continuing the ignition until a negative test for chlorine was obtained in the ignited oxide. The oxide was dehydrated by ignition in a silica vessel in dry air at 900 C.

The hydrogen was prepared electrolytically using a 15-per-cent caustic soda solution as the electrolyte and nickel electrodes. The gas was washed and dried in a train containing successively saturated silver sulphate, alkaline permanganate, solid caustic soda, concentrated sulphuric acid, palladium asbestos heated to 300 C., soda lime, concentrated sulphuric acid, "Ascarite," and phosphorous pentoxide.

The apparatus used was constructed entirely of silica and permitted a slow stream of hydrogen to pass over the oxide or metal. The oxide itself, and, therefore, the metal resulting from its reduction was enclosed in a silica bottling apparatus of the type used by Richards in some atomic weight determinations, and which permitted the opening and closing of the weighing tube without contamination from the outside.

The silica tube was enclosed in an electric furnace so constructed that the tube fitted tightly. The temperatures were measured by a platinum-rhodium thermocouple whose junction was placed directly beside the bottling tube containing the metal or oxide.

The gas issuing from the other end of the silica tube was conducted through a saturated solution of silver sulphate by means of a tube dipping just below the surface of the liquid. A "T" tube with stopcock was inserted at the end of the hydrogen train and served to introduce dry air into the system to be used for sweeping out the hydrogen.

All weighings were made using a silica counterpoise of approximately the same size and shape as the bottling tube in which the oxide was contained. The handling of the bottles was facilitated by the use of thoroughly washed and lint-free finger stalls. These permitted a more accurate handling of the weigh-

ing tubes than the usual use of tongs. They were kept in the desiccator with the counterpoise at all times.

The balance was a Troemner No. 10 which had a sensibility of 0.00002 g. The weights were calibrated by Richards' substitution method.

The procedure in every case of heating in hydrogen was as follows: The bottle containing the germanium dioxide had its stoppers removed at the moment of introducing it into the larger silica tube. Pure dry hydrogen was then allowed to pass over the material in the bottling tube for one hour to displace the air. The desired temperature was then reached and maintained for the time indicated in Table 2. At the conclusion of the heating period, the bottle was allowed to cool in hydrogen, and when cool, a stream of dry air was passed through the tube until the hydrogen had been swept out. The stoppers were then inserted tightly and the bottle was removed from the tube and placed in the dessicator. The bottle and counterpoise were allowed to come to the same temperature and surface condition side by side in the desiccator which was allowed to remain near the balance for some time before final weighings were made.

A sample of germanium dioxide prepared as described was heated to constant weight at 950° C. in a slow current of dry air, washed free from dust, carbon dioxide, and other impurities. A stream of pure hydrogen was then allowed to pass and an effort was made to cause a very gradual increase in temperature above 500° C. At this point, the surface of the well-distributed oxide was gray and when the temperature had reached 600° C., it was a very dark gray. Reduction proceeded easily, and although a dark deposit appeared in the bottling tube above the material, none of that deposit appeared outside of the containing tube. As reduction proceeded this deposit became a thin film of metal.

The reduction of 1.69443 gms. of germanium dioxide was not complete after heating in hydrogen at 600° to 624° C. for thirty-two hours for repeated weighing gave values in excess of that calculated from the initial quantity of oxide. The temperature was then raised in steps as shown below. It soon became obvious that each additional period of heating in hydrogen gave a slight loss in weight.

Attention should be called to the fact that the germanium dioxide used was an almost impalpable powder and the metal produced by the careful reduction of this oxide was, therefore, in a very fine state of division and presented a surface to the action of the hydrogen many times greater than that obtainable by pulverizing a button of the metal after melting. The table given below shows a representative experiment and justifies the conclusion that germanium metal in a very fine state of division is volatile in hydrogen at temperatures considerably below the melting point of the metal.

TABLE 2

	Grams
Weight of germanium dioxide taken	1.69443
Weight of germanium expected (Ge=72.5)	1.17556

Hours heated in hydrogen	°C.	Weight of bottle contents
8.0	595	1.23219
6.0	595	1.17636
4.5	595	1.17628
7.0	595	1.17619
6.5	595	1.17618
6.0	783	1.17602
7.5	783	1.17601
7.0	843	1.17564
4.0	843	1.17561
7.0	868	1.17544
6.5	868	1.17534
11.0	868	1.17529
6.7	890	1.17511
6.5	890	1.17505

Toward the end of the experiment, a mirror was found in the cold part of the outer silica tube where the tube projected out of the furnace. This mirror was dissolved in a mixture of freshly distilled ammonia and 30-per-cent hydrogen peroxide and the ignited germanium dioxide weighed. A blank determination on the hydrogen peroxide used gave no weighable residue. In

the manner described, 0.00026 g. of germanium was recovered. The silver-sulphate solution was analyzed for germanium, and 0.00017 g. of the metal was found.

Hydrogen Contained In Germanium Melted and Cooled In Hydrogen

An effort was made to determine whether hydrogen was contained in germanium which had been prepared by the reduction of germanium dioxide in hydrogen and subsequently melted and cooled in that gas. 1.7085 gms. of dioxide were reduced in hydrogen until the weight of metal was less than that calculated for an atomic weight of 72.5, and the metal was then melted and kept molten in this gas and finally cooled. This metal was allowed to stand in a weighing bottle in a desiccator for twenty days.

The weighed metal in globular form was introduced into a silica tube and the tube was evacuated by means of a Toepler pump. The metal was then melted and any gas pumped off during the heating and melting period was collected in an eudiometer tube over mercury. Evolved gas was first observed at 690° C., and a larger volume of gas was collected at the moment of melting of the metal. The gas collected in this manner was mixed with twice its volume of oxygen and sparked under reduced pressure. The reduction in volume was used to calculate the amount of hydrogen.

The results are indicated below:

Barometer	71.10
Weight of metal	0.64917 g.
Volume of gas collected	0.158 c.c. N. T. P.
Volume after adding oxygen	0.660 c.c.
Volume after sparking	0.479 c.c.
Volume diminution	0.181 c.c.
Volume of hydrogen	0.121 c.c.
C.c. of hydrogen per gram of metal	0.1864

Metallic mirrors were found in all cases when the metal was heated in vacuo. Slight volatilization of the germanium and a

consequent formation of metallic mirrors in the cooler part of the tube was first noticed at a temperature of 750 to 800° C.

Melting Point of Germanium in Hydrogen

During the above experiment, it was observed that germanium appeared to melt in hydrogen at a different temperature than in vacuo. These melting points were therefore investigated more carefully.

The metal which had been prepared by reduction in hydrogen as shown in Table 2 and then melted in hydrogen, was placed in a silica tube and the tube than evacuated. Pure hydrogen was then admitted to fill the tube and then pumped off. In this way the tube was washed free from air and filled with pure hydrogen at atmospheric pressure. The metal was melted and cooled in hydrogen, and one-half of it was set aside as metal No. 1. The remainder was replaced in the tube and melted in vacuo with continual pumping off of any liberated gases. This metal was cooled in vacuo as metal No. 2.

Metal No. 1 was broken into angular pieces, placed in a silica tube which was then evacuated, then filled with pure hydrogen and thus washed with hydrogen several times. Hydrogen was then admitted until atmospheric pressure obtained. Metal No. 2 similarly broken was placed in a similar tube and sealed in vacuo. The pieces of metal in each tube were kept in one end and then tapped down into the hot part of the tube as they were needed. In this way, a number of experiments could be made without reopening the tube.

The parts of the silica tube containing the pieces of metal to be melted and the thermocouple junction were fastened together with platinum wire and inserted in the well insulated electric furnace. The temperature at which the sharp-edged pieces of germanium flowed and became globules was considered as the melting point since the quantity of the metal and the arrangement of the apparatus would not permit a cooling curve to be taken. Germanium was found to have a flowing point of 958.8° C. in hydrogen at atmospheric pressure and 975.4° C. in vacuo. This experiment was repeated several times. Pieces

of pure silver were placed in the furnace along with the tubes containing the germanium and their flowing point was used as a check on the temperature. These samples melted at 961.0° C.

Melting Point of Germanium in Carbon Dioxide

Some of the metal that had been used in the above experiment was placed in a graphite crucible and covered with sugar charcoal and then melted for one hour at 1000° to 1050° C. This metal was found to have some particles of carbon in the outer surface of the cooled mass which were removed by scraping the surface. The cooled metal was broken into pieces having sharp edges but the broken surfaces showed no such particles.

The broken pieces were placed in a silica tube which was wired to a similar tube containing the thermocouple junction. The tube containing the metal was then evacuated and filled with dry carbon dioxide three times and then filled with carbon dioxide at atmospheric pressure. The metal melted at 958.0° C.

Formation of Metallic Mirrors When Germanium Is Heated in Vacuo

In every experiment with metallic germanium detailed in this paper mirrors were obtained similar in appearance to those described by Müller and Smith.[10] In order to determine whether the formation of mirrors was due to a property of the metal or to the influence of traces of germanous oxide or of hydrogen, the following experiment was made:

A portion of germanium dioxide was mixed intimately with four times its weight of pure sugar charcoal and placed in a narrow-bore silica tube closed at one end. A plug of sugar carbon equal in weight to four times that of the germanium dioxide used was next inserted and the tube evacuated. On heating, gas was evolved in large quantities but the reaction finally quieted down and the temperature was raised to 1000° C., and maintained for ten minutes. All gases evolved were pumped off

[10] Müller and Smith: *Jour. Amer. Chem. Soc.*, 44, 1909 (1922).

immediately. The cooled mixture of germanium and carbon was levigated with water and the heavier particles thus obtained were dried at 120° C., and put back in the original tube which had been cleaned thoroughly. The tube was evacuated and heated and at 760° C., a distinct mirror formed at the beginning of the cold part of the tube. Five successive mirrors with distinct boundary lines were formed by progressively pulling the tube a short distance out of the furnace. The mirrors formed during thirty minutes' heating were removed by hydrogen peroxide-ammonia mixture and the germanium dioxide obtained weighed as such. The germanium remaining mixed with carbon was placed in a weighed crucible and oxidized with fuming nitric acid; 0.00653 g. of germanium were found in the mirror, and 0.00914 g. remained mixed with carbon in the tube. It is to be noted that no hydrogen could have been responsible for the formation of mirrors in this instance nor is it likely that any germanous oxide could have been present. It is to be concluded, therefore, that germanium treated in this way shows a marked tendency to mirror formation when heated in vacuo to 760° C., or above that temperature.

A quantity of metal prepared by the reduction of germanium dioxide in hydrogen was treated in exactly the same manner as that recommended by Dennis and his co-workers,[11] repeatedly refusing the metal under a flux of carefully purified sodium chloride. The button of metal finally obtained was boiled with water, all visible traces of flux removed and the button was then fused in pure hydrogen and cooled in at atmosphere of the same gas. The ingot of metal thus obtained was broken in half. The one portion was re-fused in hydrogen in a silica tube and the tube evacuated by means of a Toepler pump while the germanium was in a state of fusion. This metal was cooled in vacuo and the tube then sealed. The second portion was placed in a similar tube in an atmosphere of pure hydrogen at normal pressure. The tubes were heated to a maximum temperature of 800° C. Successive metallic mirrors were formed in each of these tubes at the outer edge of the furnace. The mirror formation was more rapid in the case of the evacuated tube than in the case of the tube containing hydrogen as would be expected, but distinct

[11] Dennis, Tressler and Hance: *Jour. Amer. Chem. Soc.*, 45, 2037 (1923).

and successive mirrors were obtained from each of these tubes upon withdrawing them a short distance from the hot portion of the furnace. In the case of the metal heated in vacuo and prepared as described above and weighing 0.34698 g., five successive mirrors were obtained by heating to a maximum temperature of 800° C. for eight hours. The total weight of the mirrors was 0.00153 g. of metal.

In addition to the above experiments, silica tubes containing mirrors of metallic germanium deposited from germanium hydride were prepared. These tubes were treated in the same manner as that described above. The mirrors were transferred completely from the heated portion of the tube to the cooler end at a maximum temperature of 800° C., but it was noticed that some volatilization took place at a temperature as low as 600° C.

It is quite evident in these cases that volatility of the metal cannot be due to any trace of oxygen or oxide in the material used.

The Reduction of Germanium Dioxide With Germanium in Vacuo

Winkler[12] stated that germanous oxide could be made by heating germanium dioxide with germanium. Biltz[13] heated an equimolecular mixture of germanium dioxide and germanium to 1000° C. for twenty minutes and concludes that "germanium dioxide appears not to be reduced by germanium under these conditions, but seems to serve only as an absorbent for air because of its spongy nature, by virtue of which the oxidation of the germanium powder is promoted". 0.34156 g. of the germanium prepared as described earlier in this paper and therefore presenting an enormous surface, was mixed intimately with 0.49226 g. of germanium dioxide likewise very finely divided. This mixture was spread over the surface of a silica boat which was then placed in a larger silica tube. The tube was evacuated and then slowly heated in the resistance furnace. A vigorous

[12] Winkler: *Jour. Prak. Chem.*, 143 (34), 210 (1886).
[13] Biltz: *Zeit. fur Anorg. Chem.*, 72, 317 (1911).

reaction began at 800° C. with formation of a very dense black deposit directly above the boat. As the furnace assumed an even temperature throughout and the deposit grew, there was a tendency for the deposit to form toward the end of the tube but not a trace of it was observable beyond the end of the furnace as was the case always with the metallic mirrors, neither was there a sharp edge to the deposit. The temperature was kept at 800° C. for thirty minutes and the boat then cooled in vacuo and then weighed. The loss in weight was 0.22523 g. equivalent to 27 per cent of the mixture used. The deposit in the tube was treated with 1:1 hydrochloric acid and it began to dissolve immediately. After contact with the deposit for one hour, the solution was divided into two parts. An excess of ammonia added to the first portion gave an immediate precipitate of yellow germanous hydroxide and the second portion gave an immediate precipitate of the orange germanous sulphide when treated with hydrogen sulphide under pressure after first neutralizing the solution with ammonia.

The tube with some of the deposit remaining stood over night with a little dilute hydrochloric acid, and on adding a large volume of water, the remaining deposit flaked off in minute particles to give the appearance of a colloidal solution with a red tinge. On standing several days more, the reddish solution had become quite colorless and this clear solution gave a white precipitate of germanium sulphide when made 6 N. with sulphuric acid. Evidently, there had been a mixture of germanium and germanium dioxide resulting from standing and this mixture had gone over to germanium dioxide on standing in contact with air.

The original boat still containing the remainder of the original material was put back in the silica tube and the whole evacuated as before. At 800° C., a dense brownish-black deposit formed directly above the boat and only in the hottest part of the furnace. Thus it appears that germanium dioxide is reduced to germanous oxide by germanium on heating to 800° C. in vacuo.

Vapor Pressure of Germanium

Reference has been made to the appearance of metallic mirrors when germanium is heated in hydrogen, and in vacuo, and attention has been called to this property under conditions that precluded the existence of germanous oxide or the influence of hydrogen. Believing mirror formation to be a property of the metal, an effort was made to determine the magnitude of the vapor pressure itself at a temperature that was the mean of those temperatures used throughout this work. Instead of measuring the actual vapor pressure of the metal, it was considered sufficient to determine the product "Pm" in the equation $Pm = g\frac{RT}{V}$

A Dumas determination was made with an apparatus consisting of double silica bulbs on either side of a small bulb containing pure germanium and connected by means of capillary tubes. The bulbs were sealed off while in the furnace. All weighings were made with a counterpoise. Double checks were made on the weight of the germanium in the bulb by dissolving out the metal which had condensed on the walls of the bulbs when they were cooled. Ammonia-peroxide mixture was used for this purpose and the germanium dioxide produced was weighed as such after ignition. It was then dissolved in boiling water and determined as sulphide to avoid errors that may have been introduced by the action of the alkaline peroxide on the surface of the silica bulbs. In all cases, the condensed germanium could be seen in a small mirror at the point of the bulb that had been cooled first. Obviously, then, the metal had a measurable vapor pressure at the temperature of 900° C.

Experiment	Volume of bulb, c.c.	Gms. of Ge in bulb	Temperature C.	"Pm" gm. mm.
1.....	29.080	0.00023	900	7.97
2.....	27.783	0.00025	900	9.07

It will be seen that we may arrive at the mean value of 8.52 mm. for the vapor pressure of germanium if we make the reason-

able assumption that germanium is monatomic in its vapor phase at 900° C. This experiment sheds further light on the reason for the volatility of metallic germanium in hydrogen at the temperatures below its melting point and for the appearance of germanium mirrors under such varied conditions.

Metallographic Examination of Germanium Metal

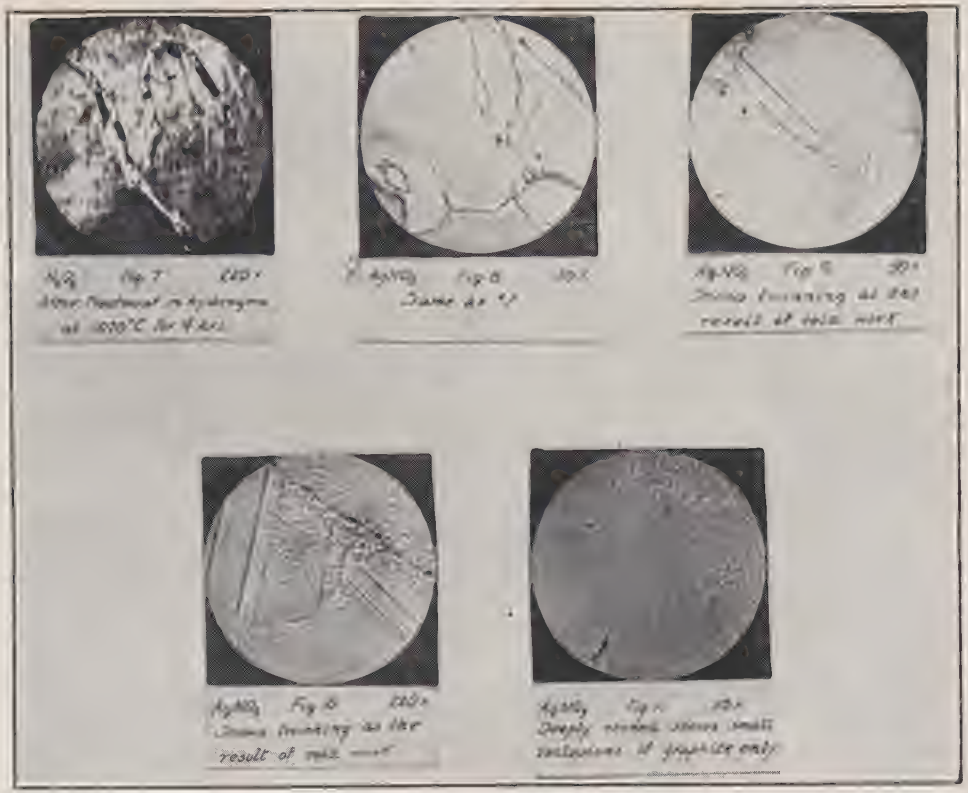
As a possible means of determining the relative purity of samples of germanium prepared by various methods, examination was made under the microscope. Samples of metal were submitted to Mr. A. K. Graham for metallographic examination. The writer takes this opportunity to express his sincere thanks for the metallographic data which appear in the following section:

Great care was taken in preparing the samples of metal for microscopic examination. After placing the samples on a flat glass surface inside a half-inch length of three-eighths-inch copper tubing and filling the tube with sealing wax, they were taken down on files and graded emery and Hubert papers in paraffin oil by hand. This oil prevented the particles of emery from becoming embedded in the metal and at the same time, enabled the samples to be polished without undue flowing or heating of the surface. The final polishing was carried out on wet wheels in the usual manner.

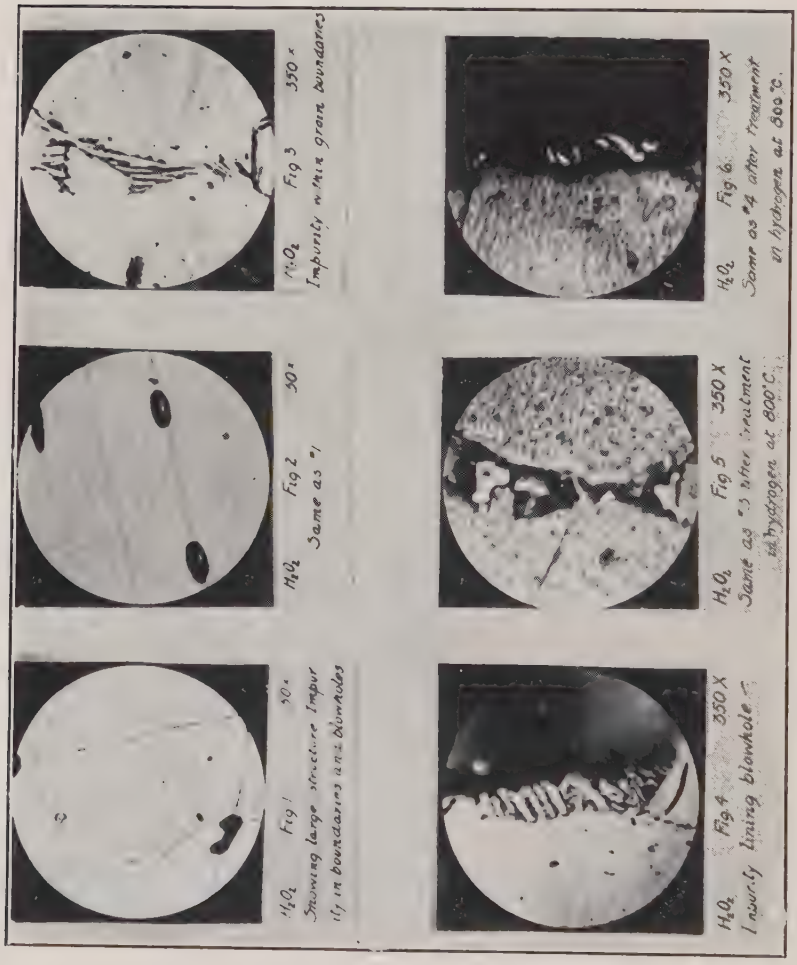
Two etching reagents were found to give satisfactory results. Ammonium hydroxide-hydrogen peroxide mixture attacked the metallic surface very slowly but uniformly, leaving the impurities for the most part unattacked and in relief. Silver nitrate also revealed the impurities and was superior in its ability to show up the grain boundaries, twinning, etc., particularly of the purer metal.

Metal prepared by the method of Dennis[14] showed a large grain structure (see Figs. 1 and 2). The grain boundaries, however, were filled with an impurity and large blow holes were visible. Segregated areas of this impurity at higher magnifica-

[14] Dennis, Tressler, and Hance: *Jour. Amer. Chem. Soc.*, 45, 2037 (1923).



Metallographic Studies


H_2O_2 Fig 1 50×
Showing large structure impurity in boundaries and blowholes
H_2O_2 Fig 2 50×
Same as #1
H_2O_2 Fig 3 350×
Impurity within grain boundaries
H_2O_2 Fig 4 350×
1 hour's living blowhole
H_2O_2 Fig 5 350×
Same as #3 after treatment at 800°C in hydrogen
H_2O_2 Fig 6 350×
Same as #4 after treatment in hydrogen at 800°C.

tion are shown in Figs. 3 and 4. This material was not readily attacked by the ammonia-peroxide reagent and had a pinkish tinge.

Figures 5 and 6 are the same as 3 and 4, respectively, and show the result of heating in a stream of hydrogen at 800° C. for thirty minutes. Either this impurity is attacked by the hydrogen or is volatile as it has lost its polished surface or nearly disappeared.

It was thought that if this material was readily decomposed by the hydrogen that subjecting the impure metal to a high temperature in a stream of hydrogen with agitation to enable the material to come to the surface would result in a much purer sample of metal. Accordingly, the metal was held at 1070° C. for four hours, in a stream of pure hydrogen for the first three hours and in vacuo for the last hour. It was then cooled in vacuo. The resulting metal was comparatively free from blow holes, but the amount of impurity seemed to have been increased.

Figure 7 shows a large inclusion of this material standing in relief practically unattacked by a very long exposure to the peroxide-ammonia reagent.

Figure 8 was etched with 10-per-cent silver-nitrate solution. It shows a larger view of the surface of this sample at a much lower magnification. The quantity of impurity is evident.

Figures 9 and 10 show a very interesting case of twinning as the result of cold work. It was recognized that the metal was brittle and could be shattered easily by a blow. As the result of cold work in preparing the surface, therefore, a number of twins were revealed. The lines shown have a definite width, and at higher magnification, it appears as though the lines themselves are the twins and not the metal between them. Several other cases of twinning were found in this sample.

One would conclude from the last experiment that either the reheating of the metal in contact with silica or reduction of the quantity of metal by volatilization were responsible for the apparent increase of the impurity. A sample of metal prepared by the careful and slow reduction of pure germanium dioxide in hydrogen and then melting in hydrogen at 1000° C. contained much less impurity as revealed under the microscope. This

sample was reheated in a graphite boat at 1200° C. for three hours in a stream of pure hydrogen, and for one-half hour in vacuo. Upon examination under the microscope, the metal showed a dense structure practically free from blowholes and impurity. Small flakes of graphite were visible, but no carbide or similar constituents was revealed. An indication of the purity of the metal was the difficulty experienced in attempting to reveal the grain boundaries. Figure 11 shows a picture of the metal at low magnification.

This last sample of metal probably represents as high a degree of purity as it is possible to obtain by the methods used. The small quantity of graphite must be regarded as a mechanical impurity. The constituent which was present in all the other samples must be reducible under the combined action of hydrogen and graphite. While it may possibly be a silicide of germanium, the writer is inclined to regard it as an oxide eutectic.

The small quantity of material available made it impossible to carry this phase of the work further.

The metal last prepared as described above and shown to be pure was subjected to the same experiments as described before under the discussion of the formation of metallic mirrors. The results were identical and metallic mirrors were formed in all cases.

Summary and Conclusions

1. The behavior of aqueous solutions of germanium dioxide with salts of the alkaline earth metals in the presence of ammonia is described and some hitherto unreported salts of germanic acid have been prepared and analyzed.

2. The hydrolysis of germanium disulphide to germanium dioxide is shown to be complete on boiling with water.

3. Some errors introduced in the estimation of germanium as sulphide have been discussed and determined.

4. Germanium, in a very fine state of division, is volatile in hydrogen at temperatures below its melting point.

5. Germanium absorbs hydrogen when it is melted and cooled in an atmosphere of that gas.

6. The melting points of germanium in hydrogen, carbon dioxide, and in vacuo are studied.

7. When heated in hydrogen or in vacuo, germanium volatilizes slightly with consequent formation of metallic mirrors.

8. Germanium dioxide is reduced to germanous oxide when heated with germanium in vacuo to 800° C. The reduction is probably not complete, but much germanous oxide is formed.

9. The product "Pm" in the equation $Pm = g\frac{RT}{V}$ was determined for germanium at 900° C., in order to throw more light on the volatility of this metal in hydrogen. Metallic germanium has been shown to have a measurable vapor pressure at 900° C.

10. The purity of samples of germanium prepared by various methods has been studied metallographically.

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